Ex. 6 - Personal Privacy

From: Engelking, Pat (MPCA)

Sent: Wed 12/11/2013 3:04:27 PM

Subject: FW: Response to Larry Baker questions about wild rice sulfate research and Wild Rice

Juvenile Seedling method

Juvenile Growth Test Sulfide Final.pdf

Hi all,

I meant to cc you on this response to the advisory committee on Larry Baker's questions in case you are interested. Thanks.

Pat

Patricia Engelking

Environmental Analysis and Outcomes

Minnesota Pollution Control Agency

651-757-2340

pat.engelking@state.mn.us

From: Engelking, Pat (MPCA)

Sent: Wednesday, December 11, 2013 8:58 AM

Ex. 6 - Personal Privacy

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Subject: FW: Response to Larry Baker questions about wild rice sulfate research and Wild Rice Juvenile Seedling method

Good morning,

| research efforts: | Not Responsive |
|--------------------|--|
| had shared with y | ou earlier. Also, please see our web page for posting of QAPPs for the various |
| sulfate research a | nd also the wild rice juvenile seedling sulfide method, which I am not sure we |
| I am forwarding a | ll of you our response to some questions Larry Baker had about the wild rice |

Pat

Patricia Engelking

Environmental Analysis and Outcomes

Minnesota Pollution Control Agency

651-757-2340

pat.engelking@state.mn.us

From: Engelking, Pat (MPCA)

Sent: Wednesday, December 11, 2013 8:52 AM

Not Responsive

Subject: Response to Larry Baker questions about wild rice sulfate research

Larry,

I'm writing to respond to your questions about the wild rice sulfate research commissioned by the MPCA that you posed in your November 19th email to me. Your questions followed the November 13th Wild Rice Advisory Committee meeting that you had not been able to attend.

You asked four questions, which we have addressed below:

1. Hydroponic study - Is sulfide being measured through the course of the incubation, to assure that it has not oxidized? Also, is pH being measured? The latter is needed to determine the form of sulfide (H2S, HS-, S2-), which I would think affects toxicity.

RESPONSE: The sulfide hydroponic exposure tests last ten days, with renewals of the hydroponic solution and sulfide spikes every two days. Yes, total sulfide is being measured in the hydroponic solution at the beginning and end of each renewal period. In addition, pH is measured at the beginning and end so that the form of the sulfide can be calculated.

2. Field survey If AVS measurements have delayed, how are the samples being preserved, and can you assure that AVS is not being oxidized during storage?

RESPONSE: The laboratory has many Acid-Volatile Sulfide (AVS) analyses to perform for the study, and analyses will not be completed until as late as February 2014. Because sulfide in lake sediment is vulnerable to oxidation if exposed to oxygen in the atmosphere, we have taken special steps to ensure that the AVS data is of high quality. In the field, the sediment is mixed and placed in a plastic sample vial under a nitrogen atmosphere, leaving a nitrogen headspace in the vial. That plastic vial is then placed in a glass bottle that is flushed with nitrogen gas, and then the combined assembly is frozen in the field on dry ice. The sample is kept frozen and unopened until subsampled for analysis by the laboratory. The plastic vial may be slightly permeable to atmospheric oxygen, which is why it is placed in a glass bottle that is flushed with nitrogen. The sediment sample is not placed directly in a glass bottle because we found that freezing the sediment in a glass bottle would sometimes crack the glass.

3. Container study. In the vertical transport model, is horizontal velocity of water across the sediments being considered? I think water flow may increase vertical diffusion by resupply sulfate more quickly than diffusion alone, and that flow may have an effect on sulfate toxicity. However, I realize the modeling to accomplish this is no longer "simple".

RESPONSE: The laboratory experiment of sulfate penetration into sediment does incorporate water movement (by aerating the overlying water) so that vertical transport is not dependent on diffusion alone.

4. In the outdoor container study, are ionic effects being evaluated? At the higher sulfate concentrations, there would be an increase in total dissolved solids, which might introduce toxicity. For example, if sulfate were being added as sodium sulfate, the increase in TDS at 300 mg SO4/L would be 443 mg/L - possibly high enough that some toxicity *might* result from ionic effects. One reference is attached; another is Goodfellow, W., et al. 2000, Major ion toxicity..., Env.Toxicol. and Chemistry 19(1): 175.

RESPONSE: Certainly one effect of the added sulfate in the outdoor container study are simply ionic effects. Because the outdoor container study has natural sediment from a wild rice lake,

the interpretation of the effects of the added sulfate is more complicated. As you know, in organic sediments sulfate can be converted to sulfide, which is very reactive. The evaluation of ionic effects would be more straightforward by examining data produced by the hydroponic experiments that evaluate the effect of added sulfate. Hydroponic experiments are a simpler system that does not have the complications of sulfate conversion to reactive sulfide and all of the associated complications.

Please let us know if you have any additional questions.

Pat

Patricia Engelking

Environmental Analysis and Outcomes

Minnesota Pollution Control Agency

651-757-2340

pat.engelking@state.mn.us